FINAL TECHNICAL REPORT

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For project entitled:

New Quantum Dot Waveguides for Nonlinear Optical Applications (An AASERT Award)

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13. ABSTRACT *(Maximum 200 words)*

Three female graduate students who are all U.S. citizens have been supported by this grant. During the past few years, this collaborative project had resulted in the preparation of CdS optical discs with the highest $X(3)$ recorded and the successful fabrication of these highest $X(3)$ recorded and the successful fabrication of these materials into waveguides. That research had also created an environment in which students could be trained not only as materials scientists but, with the exposure to the activities of the Arizona Optical Sciences Center, simultaneously as "new materials-based device fabricators." In the future, such trained students will be invaluable in rapid exploitation of new materials and technology transfer in the field of photonics. Quantum dot samples based on CdS and their fabrication into waveguides had been successfully accomplished. We proposed to adopt the same technique, that is the SOL-GEL technique, to prepare other quantum dot samples based on METAL CLUSTERS, e.g., silver and CdTe. Metal cluster quantum dots have very high $X(3)$, (2) Their containment in an oxide glass matrix and their fabrication into waveguides have not been reported. Theoretically, however, CdTe quantium dots should have higher values of $X(3)$ than CdS. We had proposed to study both metal clusters and CdTe if support was available for our students. Originally, the present ASSERT award was made for one student only. We therefore decided to conduct research on CdTe only. The plan was to use sodium borosilicate glass as a matrix as for the CdS quantum dot samples. Firstly, the sol-gel method enabled us to make dense glasses at the relatively low temperatures of 500-550 O c. Secondly, a sodium-containing glass would permit ion-exchange with potassium ions in a molten salt bath

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1. Introduction and Background

This is the final technical report of an AASERT grant award covering the period from 1 July 1995 to 30 September 1999. Three female graduate students who are all U.S. citizens have been supported by this grant.

The principal investigator had been conducting research on electronic and optical materials for many years mostly under AFOSR sponsorship. For some ten years he had been conducting research on QUANTUM DOT materials with SDIO/AFOSR support with Dr. Charles Lee of AFOSR as the program manager. That parent program, AFOSR-F-49620-94-1-0339 involved the fabrication of CdS quantum dot materials and their fabrication into devices in collaboration with Professor N. Peyghambarian of the University of Arizona. During the past few years, this collaborative project had resulted in the preparation of CdS optical discs with the highest $\chi^{(3)}$ recorded and the successful fabrication of these materials into waveguides. That research had also created an environment in which students could be trained not only as materials scientists but, with the exposure to the activities of the Arizona Optical Sciences Center, simultaneously as "new materials-based device fabricators." In the future, such trained students will be invaluable in rapid exploitation of new materials and technology transfer in the field of photonics.

Quantum dot samples based on CdS and their fabrication into waveguides had been successfully accomplished.[1] We proposed to adopt the same technique, that is the SOL-GEL technique, to prepare other quantum dot samples based on METAL CLUSTERS, e.g., silver and CdTe. Metal cluster quantum dots have very high $\chi^{(3)}$.[2] Their containment in an oxide glass matrix and their fabrication into waveguides have not been reported. Theoretically, however, CdTe quantum dots should have higher values of $\chi^{(3)}$ than CdS. We had proposed to study both metal clusters and CdTe if support was available for our students. Originally, the present ASSERT award was made for one student only. We therefore decided to conduct research on CdTe only. The plan was to use sodium borosilicate glass as a matrix as for the CdS quantum dot samples. Firstly, the sol-gel method enabled us to make dense glasses at the relatively low temperatures of 500-550°C. Secondly, a sodium-containing glass would permit

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ion-exchange with potassium ions in a molten salt bath and thus lead to the fabrication of waveguides. The concept of such a waveguide device is shown in Figure 1. Later, we requested and obtained AFOSR approval to have a no-cost extension of this AASERT grant and were able to begin work on the preparation of silver clusters. The research carried out over this entire grant period is summarized below.

2. Research Performed

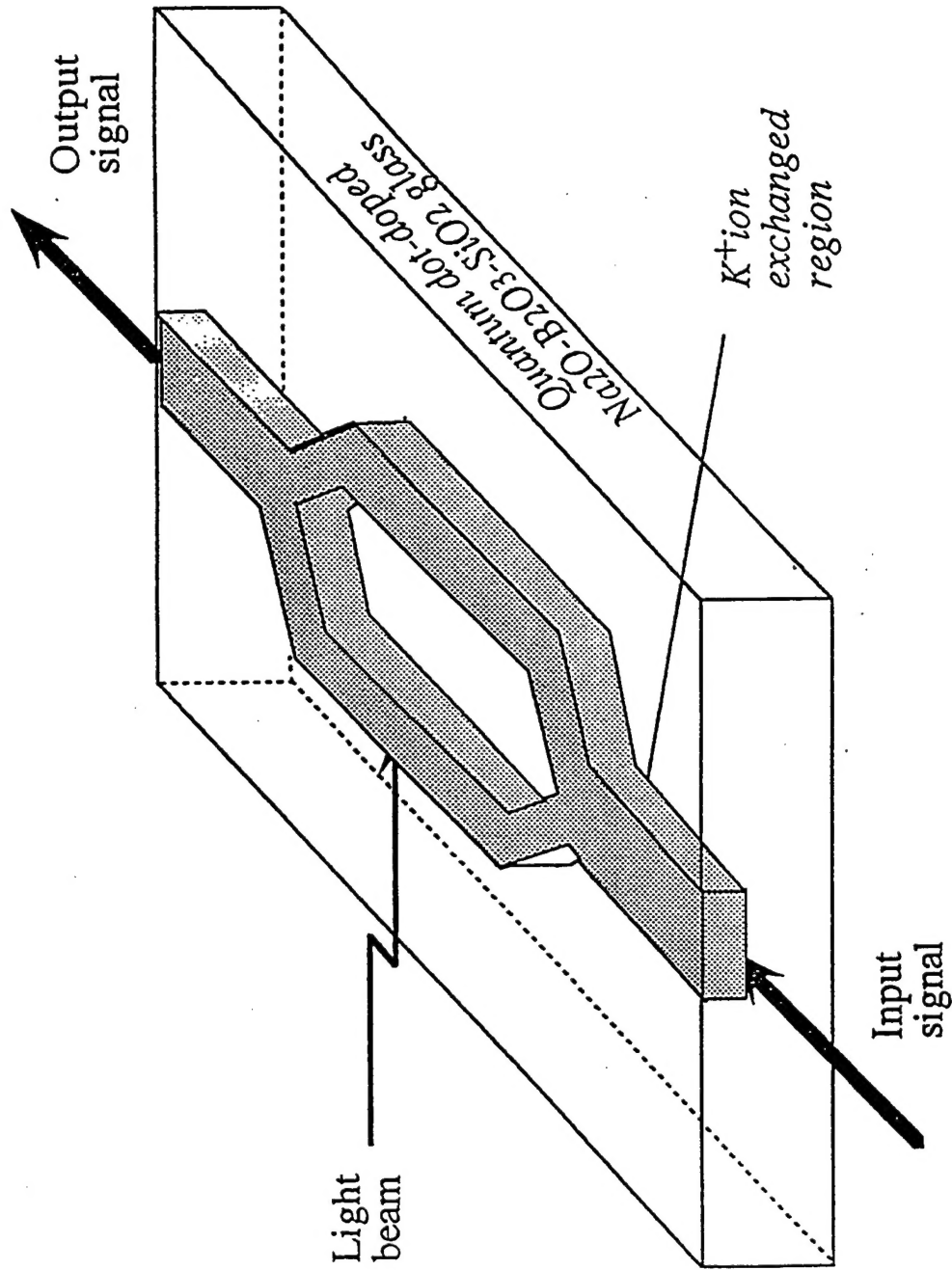### 1. CdTe Quantum Dot-Doped Sodium Borosilicate Materials

The third-order nonlinearity of quantum dots (QDs) is predicted to increase with a larger degree of quantum confinement.[3] The theory is based on a simple two-level system as shown in Eqs. (1) and (2). The enhancement of the nonlinearity due to nanocrystallite size is given by the factor $(R_e/R)^3$, where R_e and R are the Bohr exciton radius and crystalline radius, respectively.

$$\frac{\Delta n}{I} = \kappa_1 \left(\frac{R_e}{R}\right)^3 \tilde{\chi}'^{(3)} \tag{1}$$

and

$$\frac{\Delta \alpha}{I} = \kappa_2 \left[\frac{R_e}{R}\right]^3 \tilde{\chi}'^{(3)}$$

The Δn and $\Delta \alpha$ are the changes in material refractive index and absorption coefficient upon excitation with high intensity light, I. $\tilde{\chi}^{(3)}$ and $\tilde{\chi}'^{(3)}$ are normalized nonlinearities, and κ_1 and κ_2 are bulk material parameters. For the same QD size, CdTe would offer a larger degree of confinement than CdS, due to a larger Bohr exciton radius (CdTe = 75Å, CdS = 28Å). In addition, with CdTe, the emission light can be developed at other wavelengths. With this smaller bandgap semiconductor material, the exciton resonance (absorption) position can be tuned continuously up to 827 nm (the CdTe bulk absorption edge), depending on the QD size.

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Fig. 1 Third-Order Nonlinear Optical Switch

(Mach-Zehnder Interferometer)

Output signal

Light beam

K^+ion exchanged region

Quantum dot-doped Na2O-B2O3-SiO2 glass

Input signal

Light beam, I, creates a phase shift in the input signal in the left arm through the nonlinear index, n_2.

The use of commercially available CdTe colloidal particles with r ranging from 20 to 100Å was first considered. CdTe colloids were purchased from the Nanocrystal Company, 155 25th Street, Troy, New York 12180. Microscopic examination revealed the size range to be very broad and dispersion in a sol-gel solution to achieve deagglomeration was not possible. This approach was therefore abandoned and attempts made to synthesize the CdTe nanocrystallites in our laboratory.

2. *Synthesis of CdTe Nanocrystallites*

Two techniques were explored for the synthesis of CdTe nanocrystallites. The chemistry involved is shown in Figure 2. In Route (a), Na_2Te was chosen as the source of Te (due to the unavailability of H_2Te gas). Na_2Te is sufficiently soluble in methanol at room temperature (> 5g Na_2Te in 100 mls MeOH). The CdO-doped gels could presumably be soaked in a Na_2Te/MeOH solution to convert the CdO gels into CdTe gels.
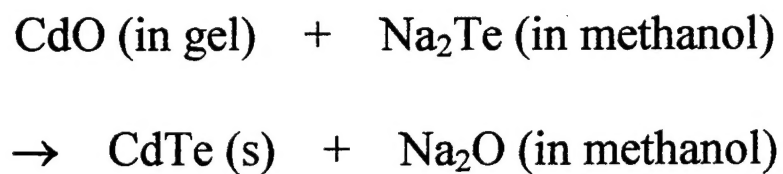
The thermodynamics for the formation of CdTe from CdO and Na_2Te were analyzed. The free energy of formation, ΔG_1^{298}, for the conversion of CdO to CdTe using Na_2Te was calculated according to the following equation:

$$CdO(s) + Na_2Te(s) \rightarrow CdTe(s) + Na_2O(s); \Delta G_1^{298} = 19.8 \text{ kcalmol}$$
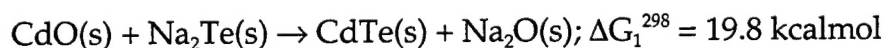
At room-temperature, the reaction is not favorable ($\Delta G_1^{298} > 0$). Unfortunately, ΔG_1 values at higher temperatures could be calculated because heat capacity data for Na_2Te was not available in the literature. Thus, the conversion reaction was experimentally tested by soaking commercial CdO powder in a Na2Te/MeOH solution at 60°C for 4 days. The solution was prepared under dry N_2 atmosphere (to prevent the oxidation of Te ions in solution to Te metal). After 4 days, the powders were separated from MeOH, and were analyzed by X-Ray diffraction (XRD). The XRD pattern of this powder showed a mixture of largely CdO and some CdTe. The three strongest CdTe peaks are all apparent, confirming that CdTe does form from CdO and Na2Te/MeOH solution after 4 days at 60°C. This implied that in the CdO-doped gel, it was possible that

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Chemical Reactions

Method (a)

$$CdO \text{ (in gel)} \quad + \quad Na_2Te \text{ (in methanol)}$$

$$\rightarrow \quad CdTe \text{ (s)} \quad + \quad Na_2O \text{ (in methanol)}$$

Method (b)

$$TeO_6^{6-} \quad + \quad 6H_2 \text{ (g)} \quad \rightarrow \quad Te^{2-} \quad + \quad 6H_2O \text{ (g)}$$

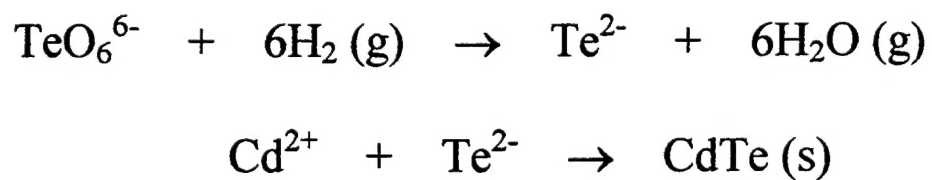$$Cd^{2+} \quad + \quad Te^{2-} \quad \rightarrow \quad CdTe \text{ (s)}$$

Fig. 2. Two techniques of preparing CdTe.

CdTe could form in the gel upon soaking at 60°C. Because the reactions were too slow, we elected to use Route (b) instead. Details for the method of Route (b) are shown in Figure 3.

3. CdTe-doped Sodium Borosilicate Glasses

Our sol-gel process was modified to fabricate CdTe QD-doped sodium borosilicate glasses. The same oxidized gel used for the synthesis of CdS QD glasses was used to fabricate CdTe QD glasses. The only significant difference was the use of a reducing gas to produce the CdTe crystals. The X-Ray diffraction of two glass samples heat-treated at 570°C for 4 hrs is shown in Figure 4. The peaks confirm the existence of CdTe crystals. Different heat-treatment conditions gave different particle sizes as shown in Tables 1 and 2. High-resolution electron microscopy confirmed that the CdTe crystals were indeed single crystals as shown in Figure 5. The linear optical absorption spectra of samples with 1 wt.%, 5 wt.% and 10 wt.% of CdTe are shown in Figure 6.

(d) Synthesis of Silver Nanoparticles in a Borosilicate Glass

The silver nanoparticles are thought not to bind directly to the glass but instead form within the pores of the glass. Thus, the choice of the matrix material is important. A borosilicate matrix (20 mol% B) was chosen for this experiment because it densifies at a much lower temperature. For sol-gel processing, this may ultimately provide a less porous structure than for a pure silica matrix. A less porous structure can have two beneficial effects. First, it may better constrain the development of the silver particles, and second, it also may better stabilize the silver nanoparticles against oxidation in the air. Sodium borosilicate glass, which is a more common matrix than pure borosilicate glass, was not chosen because the silver (Ag^+) would initially have the same charge as the sodium (Na^+). This would have unnecessarily added one more variable for consideration in the development of the particles.

Initially, silver nitrate was added to the borosilicate sol. The preparation technique is as shown in Figure 7.
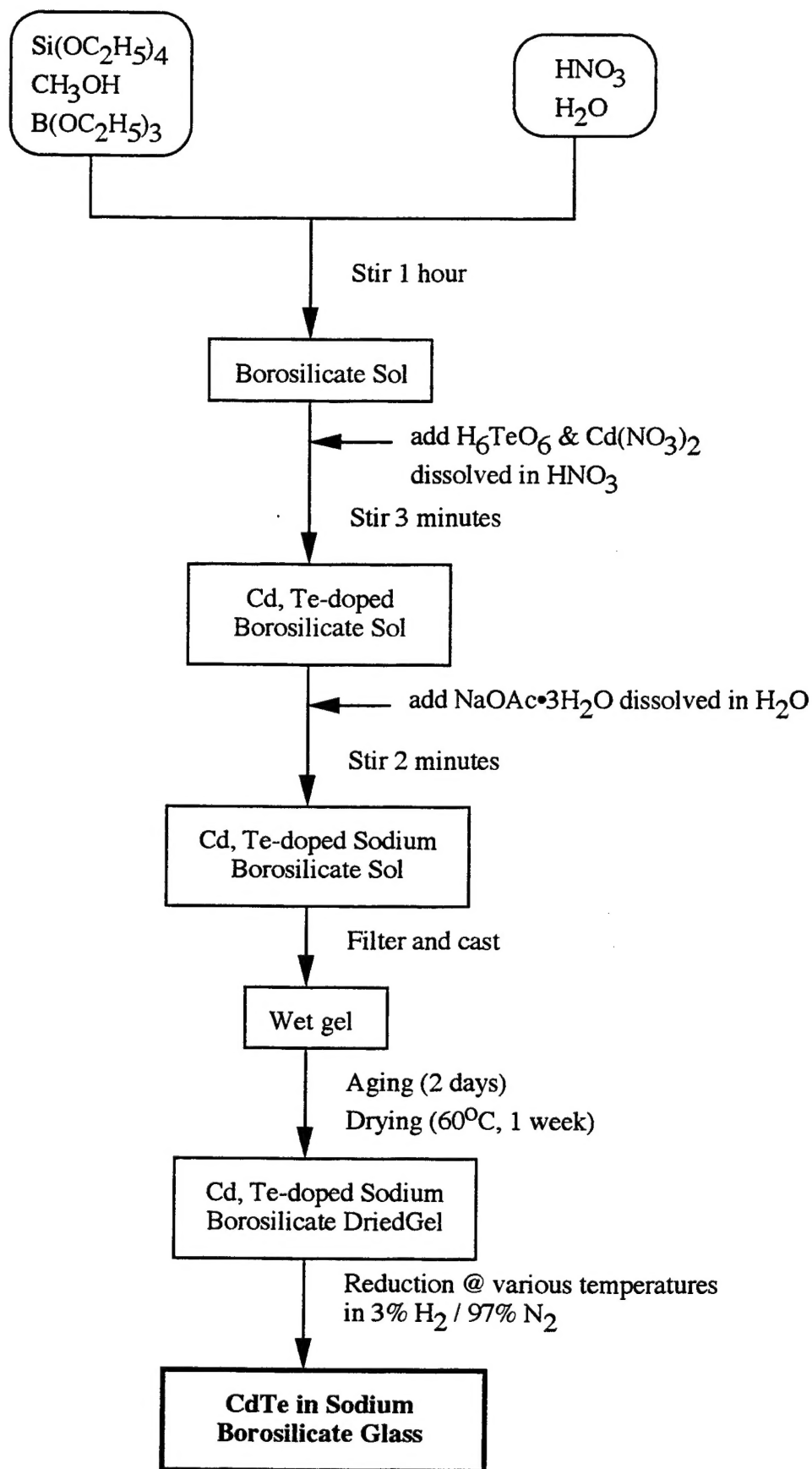
Fig. 3. Preparation of CdTe Quantum Dot-doped Sodium Borosilicate Glass by Method (b)
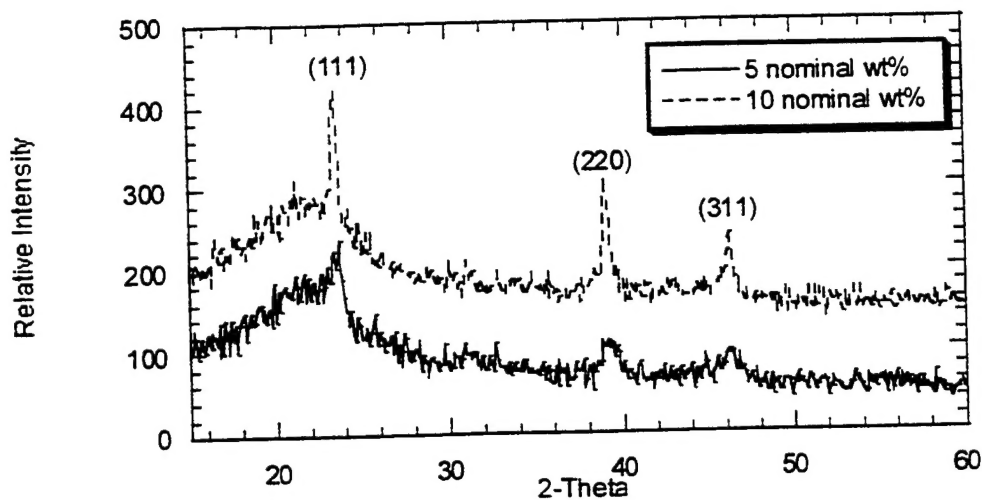
Figure 4 X-Ray diffraction patterns of 5 and 10 nominal wt.% CdTe quantum dot-doped sodium borosilicate glasses heat-treated to $570°C/4$ hrs [Reduction method]
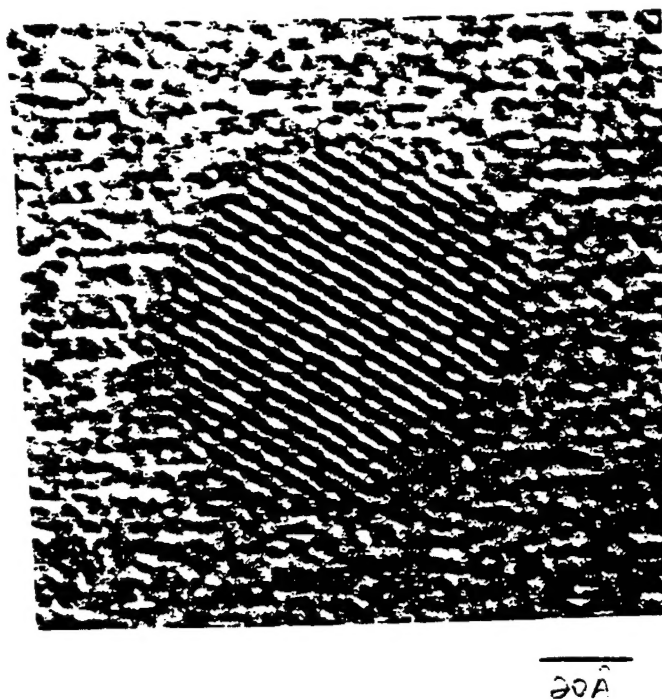

Figure 5 High-resolution transmission electron micrograph of a CdTe nanocrystallite in a 10 nominal wt.% sample in a 5 Na_2O-15B_2O_3-80SiO_2 matrix heat-treated to $540°C$ for 4 hrs in $3H_2$-$97N_2$ (vol.%)

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Table 1   Average particle size calculated by the Scherrer's equation for the different CdTe concentrations heated to 570°C/4 hrs in flowing $3H_2$-$97N_2$ (vol.%) atmosphere

CdTe Concentation (wt.%)	Average Particle Size (nm)
5	5.2
8	5.8
10	5.7

Table 2   Average CdTe particle size calculated by the Scherrer's equation for various heat-treatment temperatures. Heat-treatment time was 4 hrs in flowing $3H_3$-$97N_2$ (vol.%)

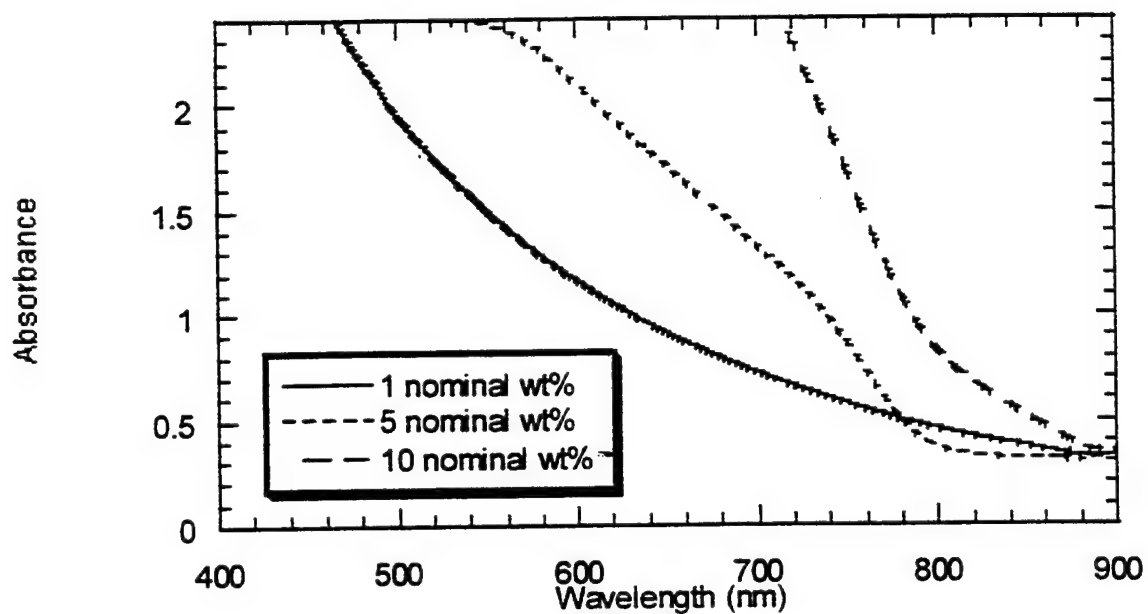| CdTe Concentration (wt.%)	Heat-Treatment Conditions (°C/hrs)	Average Particle Size (nm)
5	520°C/4 hrs	4.8
5	540°C/4 hrs	5.0
5	570°C/4 hrs	5.2
10	520°C/4 hrs	5.9
10	540°C/4 hrs	6.4
10	570°C/4 hrs	6.7

Figure 6 *Linear optical absorption spectra of different concentration CdTe-doped sodium borosilicate glasses heat-treated to 570°C/6 hrs in 3H₂-97N₂ (vol.%)*

The plot shows Absorbance (y-axis, 0 to 2+) versus Wavelength (nm) (x-axis, 400 to 900) for three curves:
- 1 nominal wt% (solid line)
- 5 nominal wt% (dotted line)
- 10 nominal wt% (dashed line)

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        ┌─────────────────────────┐
        │ TEOS                    │
        │ ethanol                 │
        │ 0.01N HNO3, aqueous     │
        └───────────┬─────────────┘
                    │  STIR 15 min
┌─────────────┐     │
│ B(OMe)3     │─────►│
└─────────────┘     │  STIR 15 min
                    │
┌─────────────────────┐   │
│ 0.01N HNO3, aqueous │──►│
│ AgNO3               │   │
└─────────────────────┘   │
                    │  MIX, CAST
                    │
            ┌───────┴───────┐
            │  Dried Gel    │
            └───────┬───────┘
                    │  FIRE in 5%H2, N2
                    │
      ┌─────────────┴──────────────┐
      │ Ag Doped  Borosilicate Glass│
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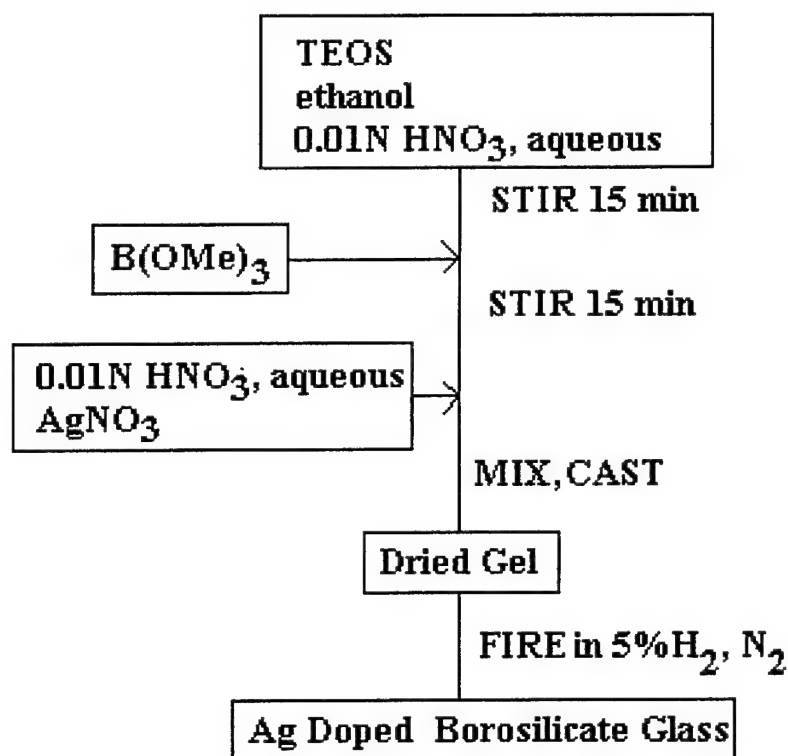
Figure 7   Preparation of silver nanoparticles in a borosilicate matrix using silver nitrate

A 5.00 wt.% Ag in borosilicate gel was dried then quickly fired at 500°C in 5% H_2, N_2 gas. An XRD of this sample showed large peaks indicative of cubic silver in the matrix. However, a TEM gave evidence of large silver particles that were near a micron in size. One source cited that this preparation method allowed spontaneous, uncontrolled growth of the particles, which resulted in some large particle sizes and thus an extended particle size distribution[4] This is not desired for the control of optical properties.

An alternative was to use a special chelating agent that would initially anchor the silver ions to the silica gel. These chelating agents, such as 3-aminopropyltiethoxysilane and N-[3-(trimethoxysilyl)propyl]-ethylenediamine

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are designed to bind metal ions and are thus naturally very basic. They react vigorously with acidic solutions. Thus, these chelating agents need to be added to basic solutions, and therefore the silver salt also needs to be soluble in a basic environment to avoid precipitation.

There are three common silver salts that have an organic anion group: silver nitrate, silver acetate, and silver citrate. It is required that the anion is organic so that it decomposes during the firing of the gel, leaving behind the silver. Of these three, silver citrate alone is soluble in a basic solution. The base used in this case is ammonium hydroxide.

The preparation technique for the silver citrate/APTES samples is as shown in Figure 8:

A DTA was performed, and it is apparent that the organic reagents leave the system at around 571°C.

The firing schedule, in reducing gas (5%H_2 in He), is shown in Figure 9.

The appearance of the gels and fired samples are as follows in Table 3:

Table 3 Prepared Samples

Wt.%Ag	Gel	Fired
0.05	clear	Glassy, clear yellow-brown
0.10	clear	Glassy, clear yellow-brown
0.25	clear	Glassy, clear orange-brown
0.50	clear	Glassy, clear red-brown
1.00	cloudy	Dull, semi-transparent brown
2.50	cloudy	Dull, semi-transparent brown
5.00	cloudy	Opaque, metallic blue

It must be noted that the 1.00, 2.50, and the 5.00 wt.% Ag samples became cloudy during the preparation, and not just after drying. Samples were also prepared with the same quantities of reagents, including the APTES, but without the addition of silver citrate. The sol did not become cloudy during preparation, but retained a clear appearance. It is assumed that the initial cloudiness of the sol is associated with the silver content and could be attributed to colloid formation.
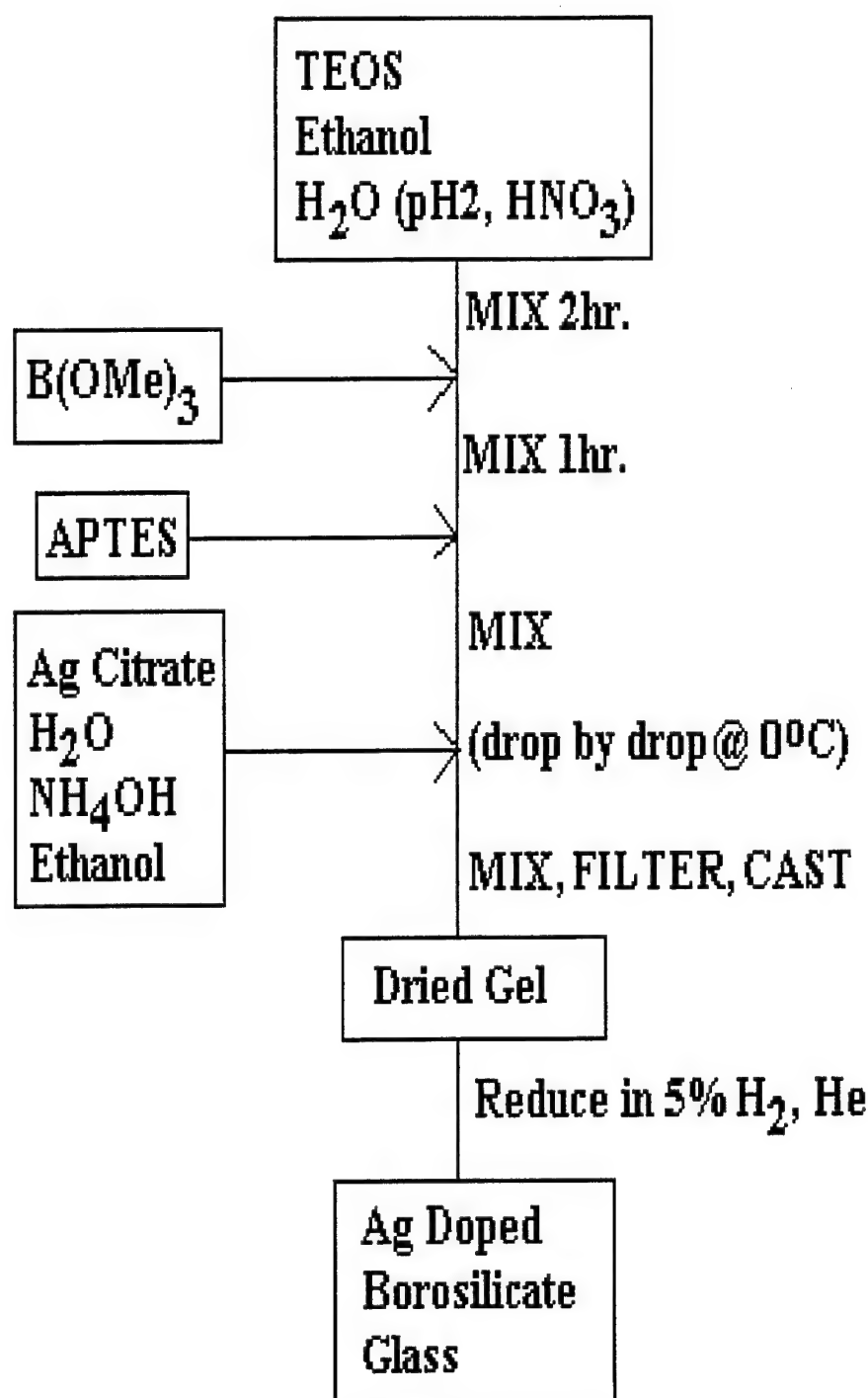
Figure 8   Preparation of silver nanoparticles in a borosilicate matrix using silver citrate and 3-aminopropyltriethoxysilane (APTES)
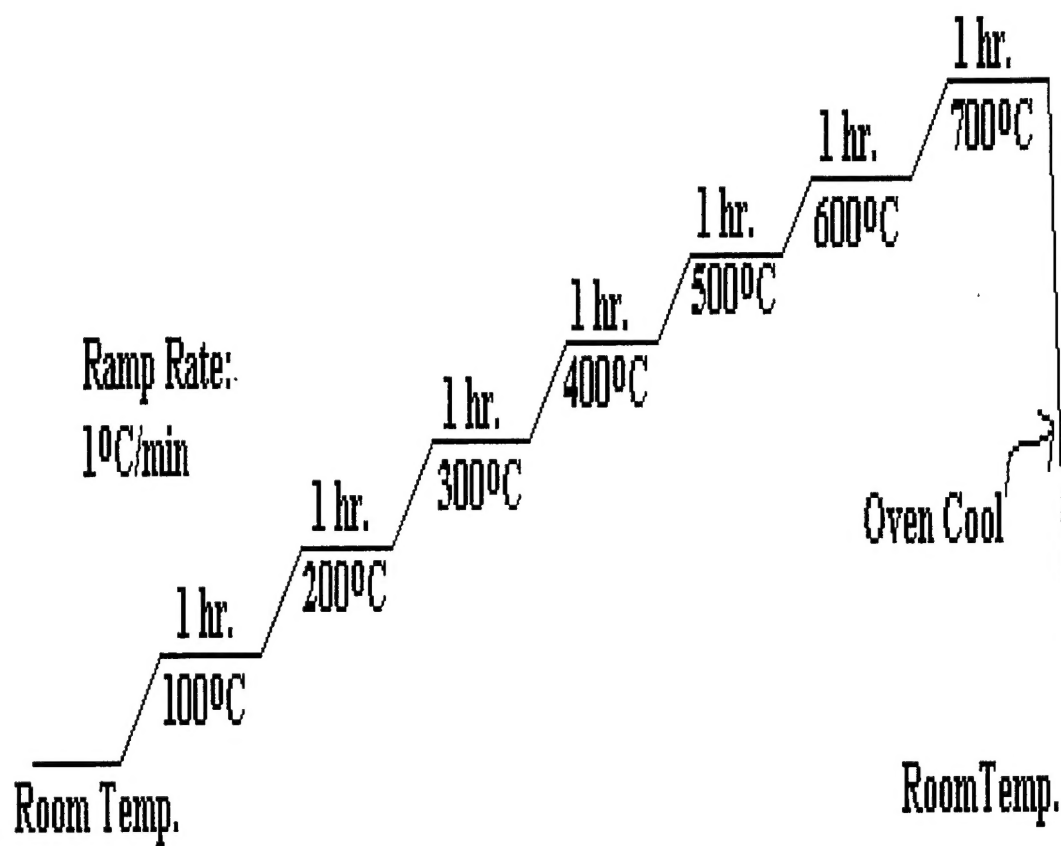
Ramp Rate:
1°C/min

1 hr.
100°C

1 hr.
200°C

1 hr.
300°C

1 hr.
400°C

1 hr.
500°C

1 hr.
600°C

1 hr.
700°C

Room Temp.

Oven Cool

Room Temp.

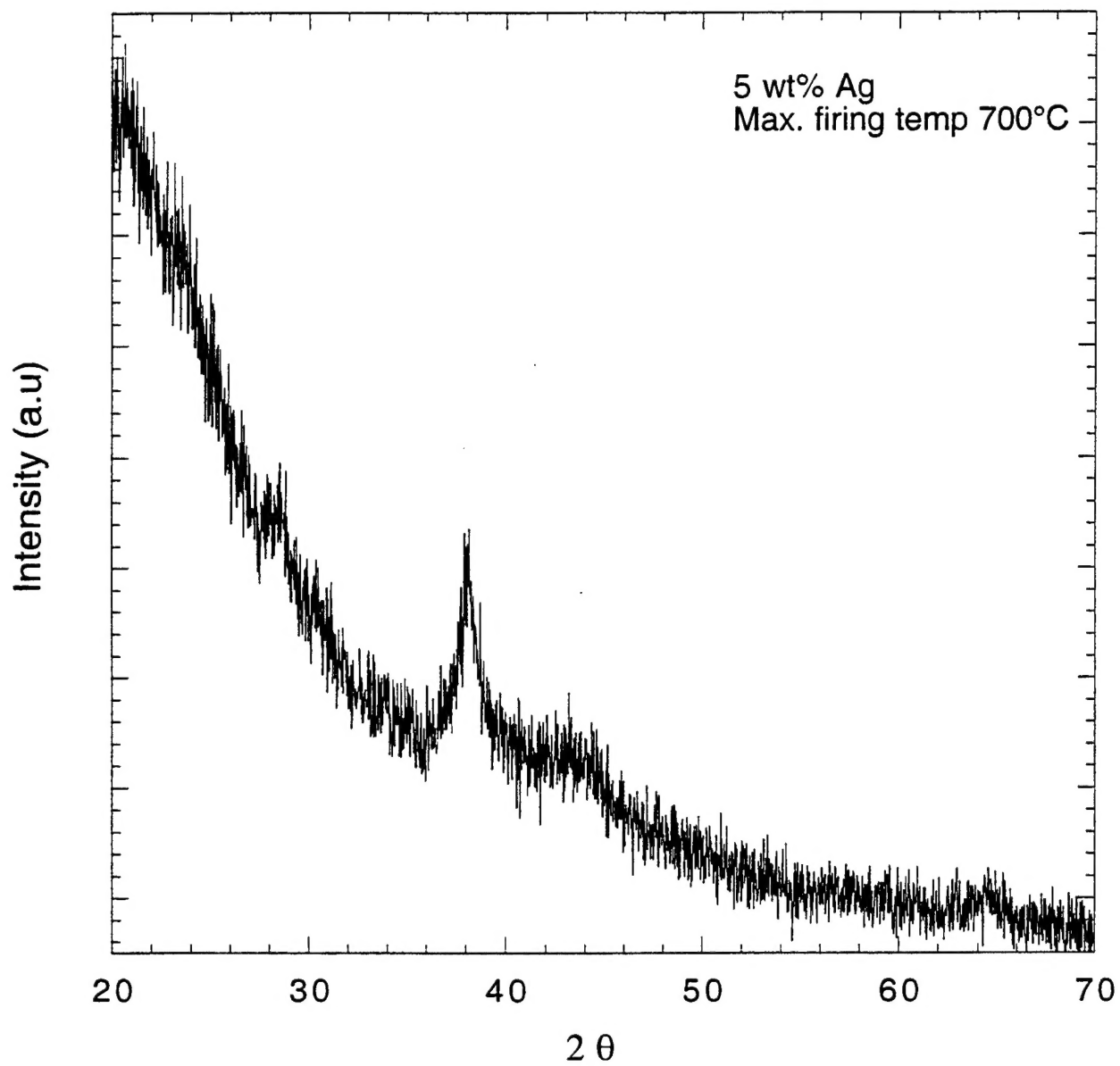**Figure 9   Firing Regimen**

5 wt% Ag
Max. firing temp 700°C

Figure 10 Silver nanoparticles in borosilicate glass

An XRD of the 5.00 wt.% Ag prepared by the silver citrate/APTES route yields strong peaks indicative of cubic silver (Figure 10). The TEM image also shows round, silver nanoparticles with a somewhat broad size distribution (Figure 11).

(e) References

1. N. Peyghambarian, et al., SPIE Proceedings **CR53**, 211 (1994).
2. J. Matuoka, et al., J. Ceram. Soc. Japan, **101**, 53 (1993).
3. L. Banyai, Y.Z. Hu, M. Lindberg and S.W. Koch, Phys. Rev. B, **38**, 8142-8153 (1988).
4. M. Menning, J. Spanhel, H. Schmidt, and S. Betzholz, Journal of Non-Crystalline Solids **174/148**, 326-330 (1992).

3. Summary

We have successfully prepared CdTe quantum dots in sodium borosilicate glass matrices. Although the research on silver clusters is not complete under the present ASSERT grant, we have been given the opportunity to initiate the research on metal quantum dots. This work is now continuing with the support from other sources. We are grateful to AFOSR for making this possible.

4. Students Trained

Ms. Lisa Kao received her Ph.D. degree and Ms. Connie Chia her M.S. degree with the support of this AASERT Grant. Ms. Sarah Robson was able to begin her M.S. research when this grant was extended. She is currently continuing her studies at UCLA for her M.S. degree.
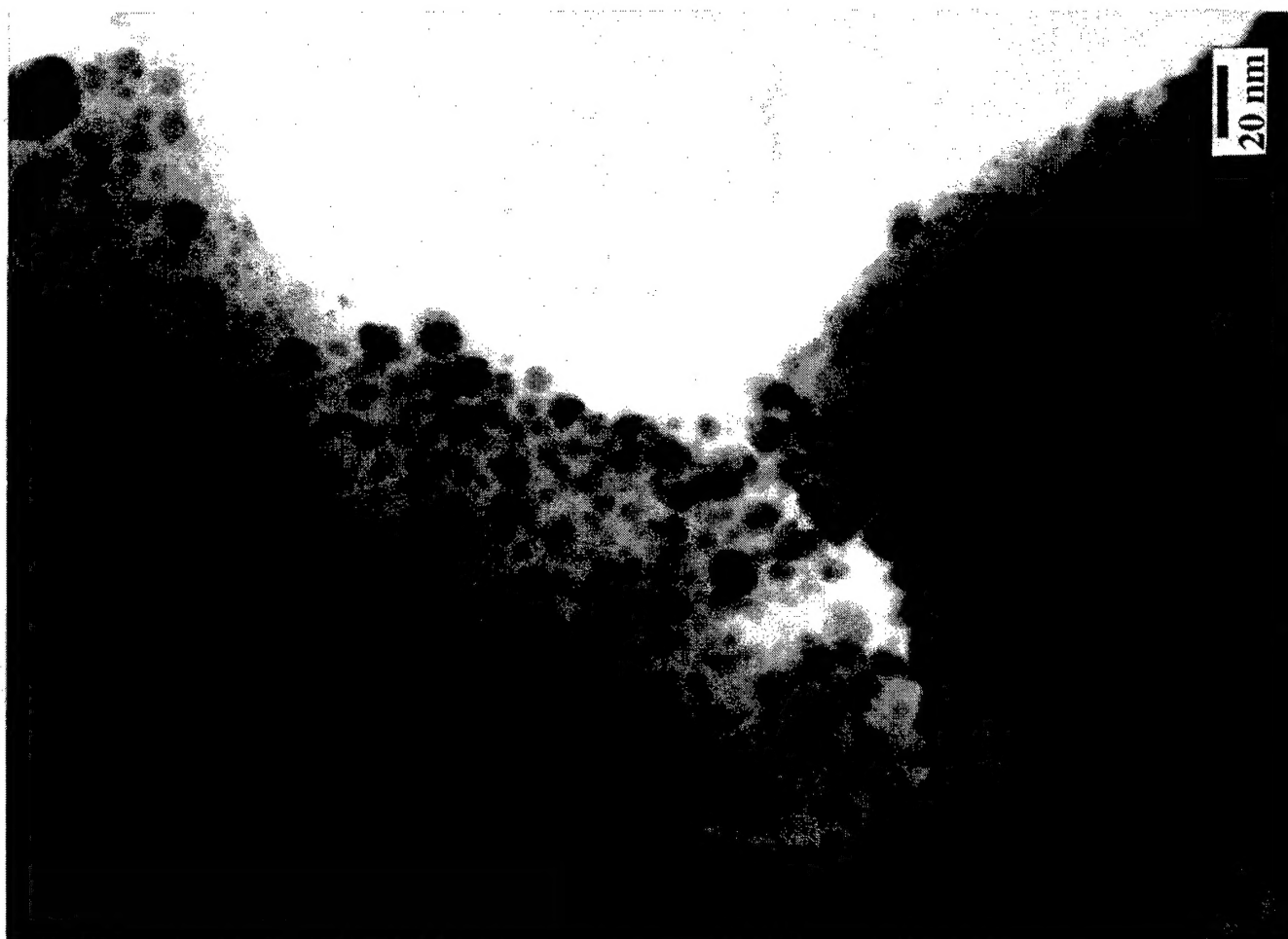
Figure 11 TEM of 5 wt.% Ag in borosilicate glass, fired at 700°C in forming gas (1 cm - 20.7 nm)